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## Optical and EPR Studies on Irradiated $\text{CdCl}_2:\text{Ag}^\dagger$

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An optical absorption band is found at 227 nm in the vicinity of the fundamental absorption edge of  $\text{CdCl}_2$  crystal doped with a small amount of  $\text{AgCl}$ . Further, there appear some absorption bands near 397 nm and 515 nm with the decrease of 227 nm band with the irradiation of  $\gamma$ -rays or neutron beam. Optical bleaching experiments show that 397 nm band decays and 227 nm band recovers with the irradiation of 350 nm light. A paramagnetic center is also found in the study of EPR spectra of the crystal irradiated with  $\gamma$ -rays or neutron beam. This paramagnetic center is identified with substitutional  $\text{Ag}^{++}$  ion with a tetragonally distorted environment in the crystal. It reveals from the investigation of isothermal decay process of the EPR and optical absorption bands that the 397 nm absorption band corresponds to  $\text{Ag}^{++}$  paramagnetic center. It becomes also clear that 397 nm band is due to the transition associated with the electron transfer from  $t_{1u}(\sigma)$  orbital of distorted  $\text{Cl}^-$  ligands to  $b_g$  orbital of the central  $\text{Ag}^{++}$  ion.

### I. INTRODUCTION

In the previous papers<sup>1,2)</sup> two of the authors reported the optical absorption and EPR spectra of  $\gamma$ -irradiated  $\text{CdCl}_2:\text{Ag}$  and discussed the thermal stability of these bands. Two remarkable optical absorption bands at 397 nm and 515 nm and also two paramagnetic centers have been found in the  $\gamma$ -irradiated  $\text{CdCl}_2:\text{Ag}$  crystal. It was proposed for their models that one of the paramagnetic centers corresponds to an  $\text{Ag}^{++}$  ion accompanied with a negative ion vacancy at the nearest neighbor site (A-center) and another paramagnetic center to tetragonally aggregated four  $\text{Cd}^{++}$  ions with an unpaired electron (B-center).

The purpose of the present paper is to report the information which has been found since that time and to discuss about the nature of optical absorption bands at 227 nm and 397 nm.

Measurements were made on  $\text{CdCl}_2:\text{Ag}$  single crystals grown by the Stockbarger method. These crystals were grown in less strained manner than the crystals which was used in the previous measurements. Non-irradiated  $\text{CdCl}_2:\text{Ag}$  crystals thus obtained have a strong absorption band at 227 nm. This band enhances as the concentration of  $\text{AgCl}$  increases and its intensity is independent of the temperature of absorption measurement.

Pure  $\text{CdCl}_2$  crystal shows the threshold of fundamental absorption at about 210 nm at liquid nitrogen temperature and no dominant absorption bands is

<sup>†</sup> Part of this work was done in the Research Reactor Institute of Kyoto University.

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observed at long wave length side up to 2000 nm.

In the EPR spectra of the irradiated  $\text{CdCl}_2 : \text{Ag}$  crystals, A- and B-bands reported by the previous papers are not observed any longer and only one kind of band exists. This new spectrum is analyzed according to a Jahn-Teller effect model of  $\text{Ag}^{++}$  ion similar to that proposed by Delbecq *et al*<sup>3)</sup>, details of which will be reported elsewhere. It is likely that this difference between the new EPR signal and A-, B-bands depends mainly upon how the imperfections are produced during the growth of single crystals.

In order to investigate a correspondence of optical absorption bands to the EPR signal, thermal bleaching experiments were carried out on irradiated  $\text{CdCl}_2 : \text{Ag}$ . Isothermal decay of 397 nm band was found to be almost parallel to that of the EPR signal. The decay process was analyzed as the first order kinetics<sup>5)</sup> and the activation energy was estimated. The 515 nm band is thermally more stable than the 397 nm band.

Optical bleaching of absorption bands was observed at room temperature by excitation with 350 nm light, where 397 nm band decreases remarkably and 227 nm band recovers. None of the optical absorption bands bleaches optically at temperatures lower than  $-10^\circ\text{C}$ .

The 397 nm band can be assigned to the electron transfer transition associated with  $\text{Ag}^{++}$  complex as discussed later in Sec. IV.

## II. EXPERIMENTAL

### II. 1. Sample Preparation

$\text{CdCl}_2 : \text{Ag}$  single crystals were grown carefully by the Stockbarger method in the evacuated quartz tube from  $\text{CdCl}_2$  chemicals containing about one mole percent of  $\text{AgCl}$ .

The  $\gamma$ -ray irradiation of the crystals were made at room temperature using the  $\text{Co}^{60}$   $\gamma$ -ray facility of the Institute for Chemical Research of Kyoto University. Irradiation dose was  $7\sim 15\times 10^6$  R. Neutron irradiation of the crystal was done at room temperature in the Kyoto University Research Reactor. Irradiation dose was about  $2\times 10^{14}$  n/cm<sup>2</sup>.

### II. 2. EPR Measurements

An usual type X-band spectrometer was used for EPR measurements. Samples were cut in the size of about  $20\times 3\times 3$  mm<sup>3</sup>. Angular variation of EPR signal was measured at liquid nitrogen temperature. For investigation of isothermal decay of EPR signals<sup>2)</sup>, measurements of EPR signal were made at room temperature.

### II. 3. Optical Absorption Measurements

Optical absorption measurements were made with a Shimadzu MPS 50L type recording spectrophotometer. Direction of incident light was parallel to the crystal *c*-axis. Measurement of thermal bleaching was done for neutron irradiated samples. As they were very hygroscopic, thermal treatment was made in vacuum glass tube in order to avoid destruction of samples. Quartz monochro-

mator or filters were used in bleaching the absorption bands with light. Optical bleaching study was performed at temperatures of 18°C, 0°C, -10°C, of dry ice and of liquid nitrogen.

### III. RESULTS

#### III. 1. EPR Spectra

Pure  $\text{CdCl}_2$  and non-irradiated  $\text{CdCl}_2:\text{Ag}$  are not paramagnetic. In the  $\gamma$ -ray or neutron irradiated  $\text{CdCl}_2:\text{Ag}$ , only one paramagnetic center is detected. The spectrum observed at liquid nitrogen temperature shows well resolved hyperfine structure at a certain orientation of crystal with respect to the direction of external magnetic field, while at room temperature the spectrum does not show any resolved hyperfine structure.

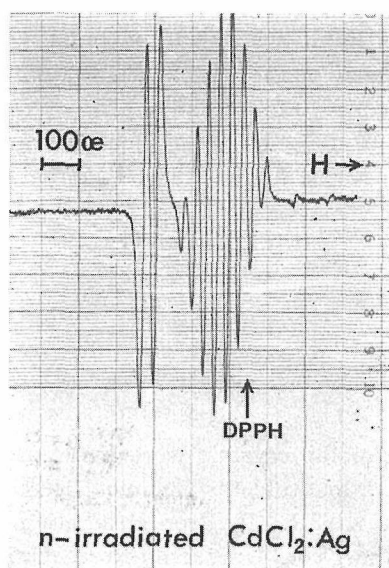


Fig. 1. EPR spectrum of  $\text{Ag}^{++}$  complex in  $\text{CdCl}_2$  at liquid nitrogen temperature, measured with an X-band EPR spectrometer. The crystal is oriented such as one of the lines joining the  $\text{Ag}^{++}$  ion and neighboring  $\text{Cl}^-$  ions is parallel to the static magnetic field.

In Fig. 1 is shown the EPR pattern with the best resolved hyperfine structure. This spectrum is analyzed according to a Jahn-Teller distortion model similar to that applied to the spectrum of  $\text{Ag}^{++}$  ion in alkali halides<sup>3,4)</sup>. Analysis of the spectrum indicates that  $\text{Ag}^{++}$  ion is surrounded with the environment of six  $\text{Cl}^-$  ions which suffers the elongated tetragonal Jahn-Teller distortion. In such a situation the symmetry at  $\text{Ag}^{++}$  ion site is lowered from  $D_{3d}$  to  $C_{2h}$  and the ground state of  $\text{Ag}^{++}$  ion splits into  $A_g$  and  $B_g$  with the latter lowest in energy.

There is discrepancy in the EPR spectra of the crystal used in the present study and that of previous one. It may be ascribed to the difference of imperfections in the crystals produced during crystal growth.

### III. 2. Optical Absorption Spectra

No absorption band is observed at the long wave length side of the fundamental absorption edge (nearly 210 nm at liquid nitrogen temperature) up to 2000 nm in pure  $\text{CdCl}_2$  crystal whether it is irradiated or not.

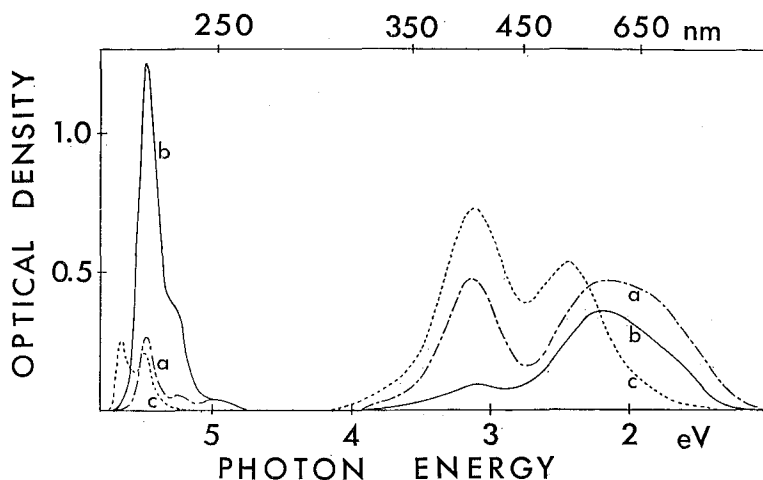


Fig. 2. Optical absorption spectra of  $\text{CdCl}_2:\text{Ag}$  measured at liquid nitrogen temperature. The fundamental and background absorption is subtracted.

- (a) The absorption spectrum of  $\gamma$ -irradiated  $\text{CdCl}_2:\text{Ag}$ .
- (b) The absorption spectrum of the  $\gamma$ -irradiated  $\text{CdCl}_2:\text{Ag}$  bleached optically with 350 nm light at room temperature for two hours.
- (c) The absorption spectrum of the neutron irradiated  $\text{CdCl}_2:\text{Ag}$ .

Curve (a) in Fig. 2 shows the absorption spectrum of  $\gamma$ -ray irradiated  $\text{CdCl}_2:\text{Ag}$  measured at liquid nitrogen temperature. New absorption bands appear at 397 nm and 500~1000 nm in addition to 227 nm and 234 nm bands which have been observed in the nonirradiated  $\text{CdCl}_2:\text{Ag}$ . Broad absorption between 500 nm and 1000 nm seems to be consisted of a number of bands. The absorption band near 700 nm enhances especially with the high dose of  $\gamma$ -ray irradiation.

Very small absorption bands appear in the vicinity of 330 nm, 245 nm and 219 nm, but they are put aside from consideration in this report because it is difficult to make sure the reproducibility of their appearance in each measurement.

Curve (c) in Fig. 2 shows the absorption spectrum of neutron irradiated  $\text{CdCl}_2:\text{Ag}$  measured at liquid nitrogen temperature. In this spectrum, peaks at 397 nm and 515 nm are dominant but the broad absorption band near 700 nm which appears in the curve (a) is not observed.

Curve (b) in Fig. 2 shows the result of the optical bleaching of  $\gamma$ -irradiated  $\text{CdCl}_2:\text{Ag}$  crystal. A  $\gamma$ -irradiated  $\text{CdCl}_2:\text{Ag}$  crystal was irradiated with 350 nm light for two hours at room temperature and absorption was measured at liquid nitrogen temperature. The intensity of 397 nm absorption band decreases and those of 227 nm and 234 nm bands increase. Optical bleaching of 397 nm band

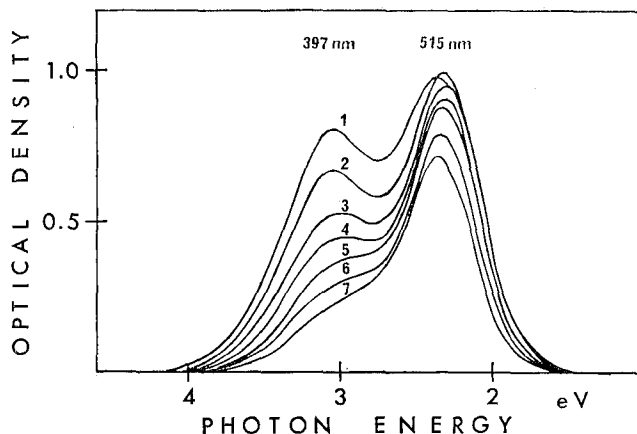


Fig. 3. Isothermal decay of 397 nm optical absorption band of the neutron irradiated  $\text{CdCl}_2:\text{Ag}$ . Annealing temperature was  $145^\circ\text{C}$  and absorption measurement was made at room temperature. Annealing time of each curve, 1) untreated; 2) 1 minute; 3) 3 minutes; 4) 5 minutes; 5) 8 minutes; 6) 13 minutes; 7) 23 minutes.

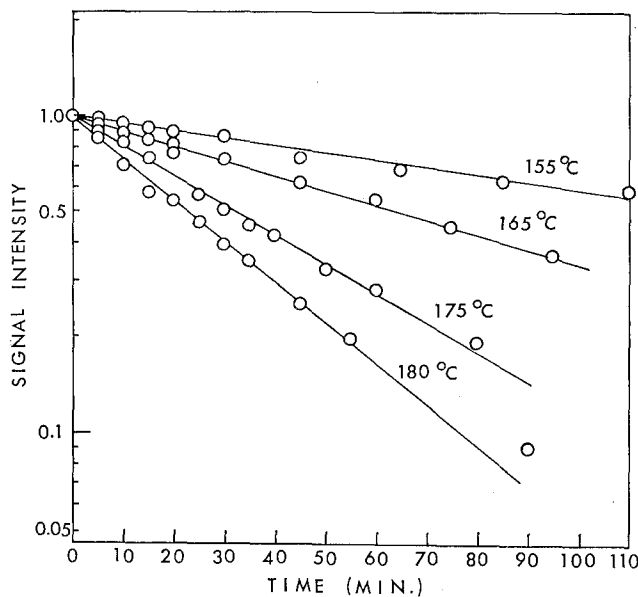


Fig. 4. Thermal decay curves of the EPR signal of  $\text{Ag}^{++}$  complex in  $\text{CdCl}_2$ . Annealing was made at temperatures of  $155^\circ\text{C}$ ,  $165^\circ\text{C}$ ,  $175^\circ\text{C}$ , and  $180^\circ\text{C}$ . Intensity measurement was made at room temperature. The DPPH was used as an intensity standard.

is possible above  $-10^\circ\text{C}$ . The activation energy of optical bleaching is estimated to be about 0.2 eV from the temperature dependence of the optical bleaching rate of 397 nm band.

### III. 3. Thermal Stability of EPR Signal and Optical Absorption Bands

Various stages of thermal decay at  $145^\circ\text{C}$  are shown in Fig. 3 for optical absorption spectra of neutron irradiated  $\text{CdCl}_2:\text{Ag}$  crystals. The 397 nm band

decays more rapidly than the 515 nm band.

In Fig. 4, isothermal decay curves of the EPR signal are shown for temperatures of 155°C, 165°C, 175°C, and 180°C. Abscissa of the graph indicates annealing time in minute. Both EPR signal and optical absorption bands are thermally more stable than that reported in the previous paper<sup>2)</sup>. This difference may be due to the fact that A-center in the previous papers has a negative ion vacancy at the nearest neighbour site of  $\text{Ag}^{++}$  ion and then charge neutrality is disturbed in the vicinity of A-center, but in the present case  $\text{Ag}^{++}$  ion is not accompanied with vacancy and can keep the charge neutrality of the center.

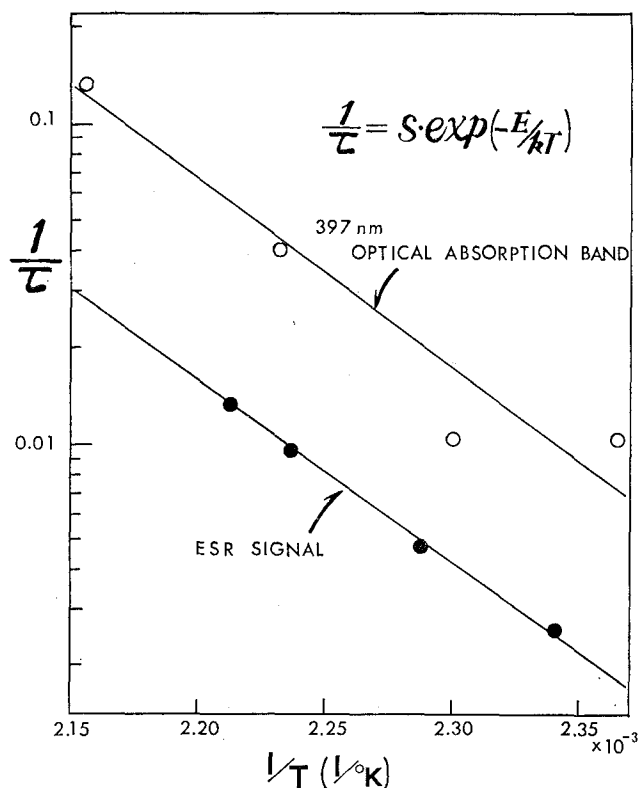


Fig. 5. The gradient of thermal decay curves as a function of reciprocal temperature. Open circles are for 397 nm optical absorption band and solid circles are for EPR signal of  $\text{Ag}^{++}$  complex, respectively.

In Fig. 5, gradient of isothermal decay curves are shown as a function of reciprocal temperature for EPR signal and 397 nm optical absorption band. Ordinate of this graph indicates gradient of isothermal decay curves, shown in Fig. 4, using reciprocal life time  $1/\tau$ . Activation energy for thermal bleaching of EPR signal is estimated to be 1.3 eV from the gradient of the line in Fig. 5 with the same procedure described previously<sup>2)</sup>. The EPR signal and 397 nm optical absorption band decay thermally with almost the same activation energy as shown in Fig. 5. Furthermore, EPR signal is not observed in the sample which has been annealed until 397 nm band vanishes, but 515 nm band remains. These facts suggest that

the 397 nm band in optical absorption spectra corresponds to EPR signal which is due to  $\text{Ag}^{++}$  ion produced in the crystal.

#### IV. DISCUSSION

##### IV. 1. Nature of 397 nm Optical Absorption Band

As described in Sec. III. 3., 397 nm band seems to be correlated closely with the EPR signal in irradiated  $\text{CdCl}_2:\text{Ag}$  crystals. It also become clear that EPR signal is due to  $\text{Ag}^{++}$  ion in the crystal converted from  $\text{Ag}^+$  ion with the action of  $\gamma$ -rays or neutron beam\*. Then 397 nm band can be attributed to a transition between certain energy levels associated with  $\text{Ag}^{++}$  ion. Possible transition for 397 nm band will be discussed below.

It is known that 15 eV is the minimum energy to be applied to an allowed transition  $(4d)^9 \rightarrow (4d)^8(5p)^1$  in free  $\text{Ag}^{++}$  ion<sup>6)</sup>. This value is too large to assign this transition to 397 nm (3.1 eV) band. Other possibilities for the nature of 397 nm band must be considered. Analysis of EPR signal shows that the wave function of unpaired hole spreads not only on the central  $\text{Ag}^{++}$  ion but also on the ligand  $\text{Cl}^-$  ions, so that and the cluster composed of  $\text{Ag}^{++}$  ion and six ligand  $\text{Cl}^-$  ions must be treated as a complex. Optical transitions within this complex may be allowed accompanying a transfer of an electron from a ligand orbital to that of central metal ion. Oscillator strength of these transitions may be nearly unity as has been pointed out by Delbecq *et al*<sup>3)</sup>.

Since the crystal has axial symmetry about  $c$ -axis as a whole and six  $\text{Cl}^-$  ions in this complex are arranged to compose tetragonally elongated octahedron through the Jahn-Teller effect, the local symmetry around  $\text{Ag}^{++}$  ion is  $\text{C}_{2h}$  and its ground state is  $\text{B}_g(x^2-y^2)$ . The  $\text{B}_g$  state has a hole in  $b_g$  orbital. Allowed optical transitions may occur from this  $\text{B}_g$  to  $\text{T}_{2u}(t_{2u}\pi)$ ,  $\text{T}_{1u}(t_{1u}\pi)$  and  $\text{T}_{1u}(t_{1u}\sigma)$  corresponding to electron transfer  $t_{2u}(\pi) \rightarrow b_g$ ,  $t_{1u}(\pi) \rightarrow b_g$  and  $t_{1u}(\sigma) \rightarrow b_g$ , respectively. Since  $t_{1u}(\sigma)$  orbital has the largest overlap with  $b_g$  orbital among these  $t_{2u}(\pi)$ ,  $t_{1u}(\pi)$  and  $t_{1u}(\sigma)$  orbitals, optical transition between  $\text{B}_g$  and  $\text{T}_{1u}(t_{1u}\sigma)$  may be most dominant and this transition may contribute mainly to the 397 nm absorption band.

As described in Sec. III. 2., activation energy of optical bleaching is 0.2 eV for 397 nm band. This energy means the amount of energy required to bleach 397 nm band thermally when the center is excited by irradiation with 350 nm light. In other words, energy of about 0.2 eV is necessary to release a hole from the excited orbital of the center (perhaps  $t_{1u}(\sigma)$ ).

It seems plausible to explain the origin of 397 nm band by the electronic transition described above. However, there still remains a questionable aspect that both the A-center and the  $\text{Ag}^{++}$  complex have optical absorption bands at 397 nm, though the former is accompanied with a negative ion vacancy and the latter is not accompanied with any defect.

In spite of above discussion, it remains still a possibility that 397 nm band is due to a certain counter product of (electron center)  $\text{Ag}^{++}$  center produced by  $\gamma$ -ray or neutron irradiation.

\* Detailed analysis of EPR signal will be published elsewhere.



#### IV. 2. Nature of 227 nm Optical Absorption Band

The 227 nm optical absorption band appears in the spectrum of  $\text{CdCl}_2$  doped with  $\text{AgCl}$  and its intensity increases with  $\text{AgCl}$  concentration. The EPR signal cannot be observed in the crystal in which optical absorption spectrum has only the 227 nm band. These facts show that 227 nm band may be due to a certain center associated with  $\text{Ag}^+$  ion in the crystal. By  $\gamma$ -ray or neutron irradiation the 227 nm band diminishes and some new bands appear at 397 nm and 515 nm complementally. The 227 nm band recovers by optical bleaching of the 397 nm band which is due to  $\text{Ag}^{++}$  center as described above. These facts are consistent with above discussion about 227 nm band.

As to the nature of the optical transition of 227 nm band, several mechanisms can be imagined as described below.

(1) Transition from  $S(4d)^{10}$  to  $D(4d)^9(5s)^1$  of  $\text{Ag}^+$  ion :

This transition is forbidden in free  $\text{Ag}^+$  ion. In alkali halide crystals doped with  $\text{Ag}^+$  ions, several weak phonon-assisted transitions are reported<sup>7,8,9)</sup>. They are those from  $(4d)^{10}$  to  $(4d)^9(5s)^1$  and their intensity enhances with increasing temperature. In the case of 227 nm band in  $\text{CdCl}_2:\text{Ag}$ , its intensity does not depend on temperature. This means that the model (1) does not hold.

(2) Transition from  $(4d)^{10}$  to  $(4d)^9(5p)^1$  of  $\text{Ag}^+$  ion :

This transition is allowed in free  $\text{Ag}^+$  ion. Absorbed energy in this transition of free  $\text{Ag}^+$  ion is known to be about 10 eV<sup>6)</sup>. This value is too large to assign 227 nm band to this transition.

(3) Perturbed exciton of  $\text{CdCl}_2$  by the substitutional  $\text{Ag}^+$  ion :

Kojima *et al.*<sup>9)</sup> concluded that  $g$ -bands in alkali halide crystals doped with  $\text{AgCl}$  are perturbed exciton bands, in other words, they arise from an electron transfer from neighboring halogen ions to  $\text{Ag}^+$  ion. However, in the case of  $\text{CdCl}_2$  this perturbation may shift the exciton band to the short wave length side of intrinsic exciton band at 6.4 eV in contrast with the case of alkali halides. Further consideration is necessary about this model.

(4) Transition associated with a  $\text{Ag}^+$  pair :

To examine this model, it is necessary to know the dependence of the intensity on the concentration of  $\text{Ag}^+$  ions. This remains as to be studied further.

(5) Allowed transition in  $\text{Ag}^+$  ion with a defect :

If the  $\text{Ag}^+$  ion is accompanied with certain defect in the crystal and loses its inversion symmetry,  $p$ -orbital of  $\text{Ag}^+$  ion may mix with  $d$ -orbital and forbidden may break. The EPR signal shows that  $\text{Ag}^{++}$  ions converted from  $\text{Ag}^+$  ions are not accompanied with any defect. The conversion process of  $\text{Ag}^+$  ions to  $\text{Ag}^{++}$  is not clear at this stage. The possibility of this model is an open problem.

Reflecting discussions on these models, it is necessary to further the study on this point of interest.

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